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# CRYSTAL GROWTH AND ROUGHENING OF SOLID D<sub>2</sub>

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## ABSTRACT

Near the triple point, growth shapes of vapor deposited hexagonal close packed D<sub>2</sub> crystals reveal two crystal orientations contain facets which persist up to the melt. This observation is in contrast with previous experiments on rare gas solids and H<sub>2</sub> where the highest T<sub>r</sub> measured is 0.8 T<sub>tp</sub>.

## INTRODUCTION

At temperatures much lower than the melting temperature, crystal facets are microscopically flat, with the exception of thermal defects. At higher temperatures, the entropy term in the surface free energy becomes larger than the surface tension term which dominates the low temperature equilibrium shape of small crystals. When this occurs, the nucleation energy barrier vanishes giving rise to long wavelength fluctuations in the surface height. The roughening transition temperature, T<sub>r</sub><sup>i</sup>, separates these two phases for each crystal face, i, such that the i<sup>th</sup> flat plane transforms into a smoothly curved surface as the temperature increases through T<sub>r</sub><sup>i</sup>. Thus, below T<sub>r</sub><sup>i</sup> the growth velocity, v<sup>i</sup>, depends exponentially on supersaturation, σ, due to the 2D nucleation required for growth, and above T<sub>r</sub><sup>i</sup>, v<sup>i</sup> depends linearly on σ due to the large number of sites available for molecules to attach<sup>1</sup>.

Smooth and uniformly thick (≈100 μm) deuterium-tritium (D-T) layers on the interiors of 1-to-3 mm diameter spherical capsules are required for ignitable inertial confinement fusion (ICF) targets for the National Ignition Facility.<sup>2,3</sup> We have previously shown that the D-T surface structure is a function of the distribution of crystallite sizes, orientations, etc. which are largely determined by the initial nucleation, growth, and surface stress tensor. A knowledge of the solid hydrogen surface stress is required to determine surface roughness limits of these D-T layers. We present the first crystal growth

morphology data, crystal growth velocity data, and estimates of the surface stress for solid deuterium.

The face centered cubic (fcc) rare gas solids, neon, argon, krypton and xenon, all have their highest T<sub>r</sub><sup>i</sup> below their respective triple point temperatures, T<sub>tp</sub>. Calorimetry data for Ar and Ne by Zhu and Dash,<sup>4,5</sup> and the observation of shape change of Xe and Kr crystals from faceted to round by Maruyama<sup>6,7</sup> both find T<sub>r</sub> ≈ 0.8 T<sub>tp</sub> for the highest transition. One roughening transition has been observed in solid H<sub>2</sub> at 0.75T<sub>tp</sub> by extrapolating critical points for successive mono-layers formed on MgO substrates.<sup>8</sup> This T<sub>r</sub> may be for an fcc H<sub>2</sub> lattice since multi-layer films of D<sub>2</sub> on MgO are fcc.<sup>9,10</sup> These results suggest that above 0.8T<sub>tp</sub>, H<sub>2</sub> and D<sub>2</sub> crystals should grow completely rounded.

The most complete set of roughening transition data comes from <sup>4</sup>He crystals where three distinct facets, (1 $\bar{1}$ 01), (10 $\bar{1}$ 0), and (0001) have been observed to roughen.<sup>11</sup> These transitions are ordered as T<sub>r</sub><sup>(1 $\bar{1}$ 01)</sup> = .3K < T<sub>r</sub><sup>(10 $\bar{1}$ 0)</sup> = .9K < T<sub>r</sub><sup>(0001)</sup> = 1.3K. Because the <sup>4</sup>He lattice structure is hcp and the molecular potential is similar to that of D<sub>2</sub>, the D<sub>2</sub> T<sub>r</sub><sup>i</sup> are expected to follow the same ordering according to the crystal plane as <sup>4</sup>He.

We have observed that two perpendicular facets on the crystal growth shapes of vapor deposited hexagonal close packed D<sub>2</sub> persist up to T<sub>tp</sub> = 18.73K. We argue below that these two orientations are the (0001) and (10 $\bar{1}$ 0) faces. Hence we conclude T<sub>r</sub><sup>i</sup> > T<sub>tp</sub> for these two orientations.

## EXPERIMENTAL SETUP

A cross sectional view of the low temperature crystal growth cell is shown in figure 1. The cell consists of two concentric copper blocks separated by a small gap, each of which has a germanium resistance or silicon diode thermometer and an electric heater connected to it. Thin disks of diamond turned copper or <111> cut Si were

placed on the center copper block providing a smooth substrate for the growth surface. A fill line enters the cell above the outer copper block, and a sapphire window on the top of the cell allows optical access. A capacitance manometer just outside the cell enables monitoring of the vapor pressure. A HeNe laser ( $\lambda = 632.8$  nm) is used in a Michelson interferometer to help determine facet orientation. Each fringe signifies a height change of  $\lambda/2(n-1) = 2\mu\text{m}$ , where  $n = 1.16$  is the index of refraction for solid  $\text{D}_2$ . The  $\text{D}_2$  gas was high purity research grade, 99.8% pure, and had a  $J=1$  concentration of about 33%.

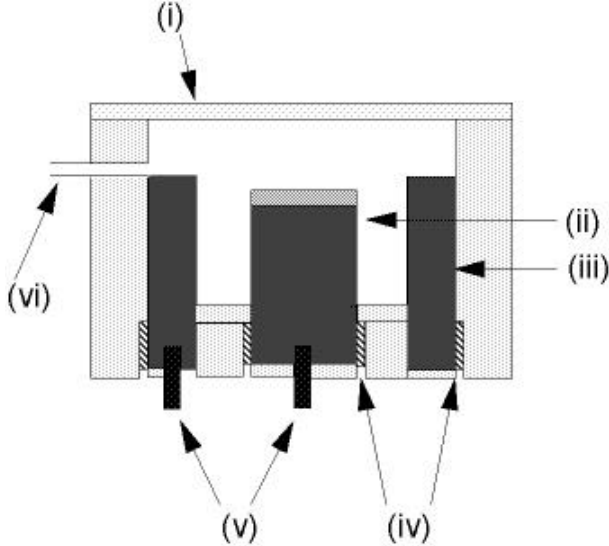


FIG. 1. Diagram of growth cell. (i) is the sapphire window for optical access. (ii) is the growth substrate, (iii) the supply substrate. (iv) are electric heaters connected to the supply and growth substrates. (v) are germanium resistance (growth morphology) or silicon diode (growth rate) thermometers. (vi) is the fill line.

To grow crystals for morphology experiments, a temperature difference between the center and outer blocks forces  $\text{D}_2$  initially deposited on the outer block to evaporate and recondense on the inner substrate. Additionally, for growth velocity experiments, large single crystals were grown by first nucleating small crystals and then applying a known constant supersaturation by slowly adding gas to the cell. Both methods provide controlled growth of crystals. The supersaturation for these experiments was  $0.03\% < \sigma < 0.2\%$ , low enough to reduce kinetic effects during growth. Kinetic roughening occurs below  $T_r^i$  when  $\sigma$  is large enough that the net flux of molecules arriving at the surface exceeds the ability of the surface to come to equilibrium.

## RESULTS

A  $\text{D}_2$  crystal slowly growing at 18.72K,  $10 \pm 5$  mK below  $T_{tp}$ , is shown in figure 2. The large flat face parallel to the substrate indicates a very stable crystal plane near

$T_{tp}$ . Although the orientation of this crystal cannot be uniquely determined by inspection, because the (0001) plane has the highest attractive energy of the hcp lattice, the Wulff construction indicates that the (0001) plane has the largest equilibrium facet size. This observation suggests  $T_r^{(0001)}$  is greater than  $T_{tp}$ .

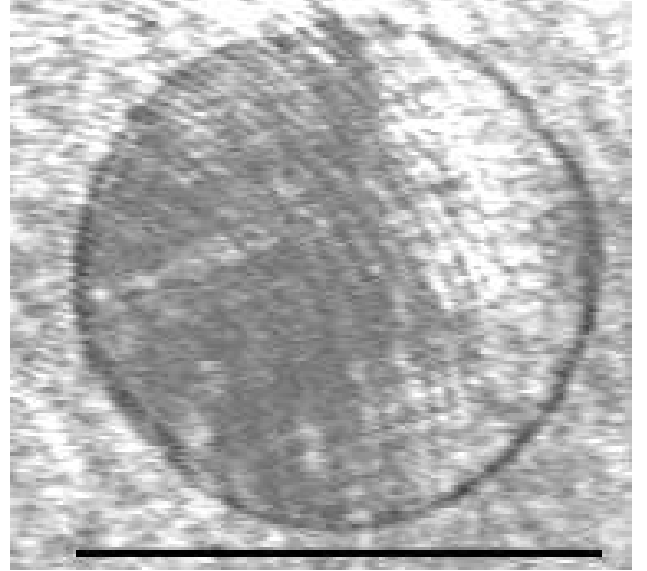


FIG. 2. A  $\text{D}_2$  crystal grown at 18.7 K. The large flat face parallel to the substrate is the (0001) plane. One interference fringe is visible on the crystal, indicating a tilt of not more than  $0.5^\circ$ . The bar in the figure is  $475\mu\text{m}$ .

Figure 3 shows the crystal shape observed most often for low supersaturation in our experiments with  $\text{D}_2$ ,  $20 \pm 5$  mK below  $T_{tp}$ . This crystal has two facets, one which makes an angle of  $65^\circ \pm 5^\circ$  with the substrate and faces the top of the page, and the second which is inclined  $30^\circ \pm 5^\circ$  to the substrate and faces the bottom of the page. These two facets are separated by the rounded surface on the top of the crystal rather than meeting at a sharp edge. This shape has been observed for a number of crystals grown under similar conditions, where the angle between the two faces varies between  $65^\circ$  and  $130^\circ$ , and the average angle is  $85^\circ$ . Again, because it is the most stable crystal plane, one of these two orthogonal facets is the (0001) plane. The perpendicular plane is either the  $(11\bar{2}0)$  or  $(10\bar{1}0)$  plane since the second plane cannot be uniquely determined from the crystal orientation. However, because the interplanar spacing is smaller, the  $(11\bar{2}0)$  plane should roughen at a lower temperature than the  $(10\bar{1}0)$ , and hence the second facet may be the  $(10\bar{1}0)$  plane.

The  $(10\bar{1}0)$  is a higher energy per area plane than the (0001) and thus should grow faster. Hence, by measuring the growth velocity of crystals similar to the one in figure 3, a preliminary assignment of the crystallographic orientation can be made. For crystals grown within 40 mK

of  $T_{tp}$  and with the two faces separated by about  $90^\circ$ , the growth velocities for  $(10\bar{1}0)$  and  $(0001)$  are  $0.006 \pm 0.0005 \mu\text{m/s}$  and  $0.003 \pm 0.0005 \mu\text{m/s}$  respectively, at  $\sigma = 0.06\% \pm 0.04\%$ . Increasing  $\sigma$  to  $0.15\% \pm 0.05\%$ , the growth velocities are  $0.006 \pm 0.0005 \mu\text{m/s}$  and  $0.07 \pm 0.005 \mu\text{m/s}$ . These results enable the planes to be labeled as shown in figure 3.

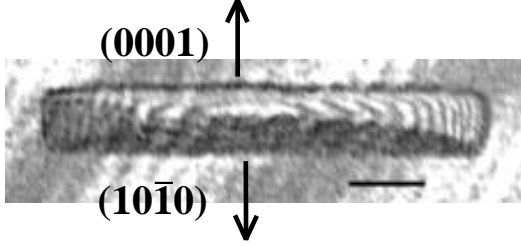


FIG. 3.  $D_2$  crystal with a different orientation than figure 2 at 18.7 K. The  $(0001)$  and  $(10\bar{1}0)$  planes face the top and bottom of the page respectively. The bar is  $100 \mu\text{m}$ .

To be sure that  $D_2$  crystals grown on the fcc Si substrate were hcp, Raman spectroscopy was used on  $[J=1] < 7\% D_2$ . The  $J = 2 \rightarrow 0$  spectrum is split into a triplet for an hcp lattice, and a doublet for fcc.<sup>12,13</sup> The observed spectrum indicates  $D_2$  crystals grow hcp on the Si substrate.

## $D_2$ SURFACE STRESS

Roughening transition theory relates the surface stress of a crystal plane,  $\sigma_S^i$ , to  $T_r^i$  by<sup>11,14</sup>

$$T_r^i = \frac{2\sigma_S^i d_i^2}{\pi k_b}, \quad (1)$$

where  $k_b$  is the Boltzmann constant, and  $d_i$  is the periodicity of the lattice planes. Although both the  $(0001)$  and the  $(10\bar{1}0)$  faces appear stable near  $T_{tp}$ , in order to place lower bounds for surface stresses in  $D_2$ , we use 18.73K as a lower bound for  $T_r^{(10\bar{1}0)}$ . In order to estimate  $T_r^{(0001)}$  for  $D_2$ , we use the the hcp  $^4\text{He}$  roughening transitions to scale from  $T_r^{(10\bar{1}0)}$ . The ratio of  $T_r^{(0001)}$  to  $T_r^{(10\bar{1}0)}$  for  $^4\text{He}$  is 1.36,<sup>11</sup> which places  $T_r^{(0001)}$  at 25 K for  $D_2$ . Then using  $d_{(0001)} = 0.294 \text{ nm}$ , and  $d_{(10\bar{1}0)} = 0.313 \text{ nm}$ , lower bounds for the surface stresses are  $\sigma_S^{(0001)} = 6.2 \text{ ergs/cm}^2$ , and  $\sigma_S^{(10\bar{1}0)} = 4.1 \text{ ergs/cm}^2$ . These are in reasonable agreement with the value of the surface tension in liquid  $D_2$  of  $3.8 \text{ ergs/cm}^2$ .

## SUMMARY

In conclusion,  $D_2$  crystals contain facets that persist up to  $T_{tp}$ , which is much higher than expected from previous  $T_r$  measurements on rare gas solids,  $T_r \sim 0.8T_{tp}$ . It is important to determine whether the lattice structure,

molecular rotation, or quantum effects cause the large differences in crystal growth. Future studies will examine substrate, molecular rotation, and isotope effects on the crystal growth shape. We will investigate the possible presence of a quasi-liquid layer on crystals from the geometry and growth rates of roughened surfaces.

## ACKNOWLEDGMENTS

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